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(54) **Curable compositions of fluoroelastomers containing bromine**

Härtbare Fluoroelastomerzusammensetzungen, Brom enthaltend

Compositions d'élastomères fluorés durcissables contenant du brome

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(56) References cited:
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Description

[0001] The present invention relates to fluoroelastomers curable compositions. More particularly the present invention relates to curable compositions of fluoroelastomers containing bromine.

[0002] Various types of fluoroelastomers are known in the art, which are widely used in all those fields where optimal elastic properties associated with high chemical and thermal stability are required. For a broad treatment of such products see for instance "Ullmann's Encyclopedia of Industrial Chemistry", vol. A-11, pag. 417-429 (1988, VCH Verlagsgesellschaft). They are copolymers based on vinylidene fluoride (VDF) and/or on tetrafluoroethylene (TFE), wherein such monomers are copolymerized with other fluorinated ethylenically unsaturated monomers, such as hexafluoropropene (HFP), perfluoroalkylvinylethers (PAVE), chlorotrifluoroethylene (CTFE) and the like, or also with non fluorinated monomers having ethylene unsaturation, such as ethylene and propylene.

[0003] The fluoroelastomers can be ionically cured by addition of suitable curing agents (for instance polyhydroxylic compounds, such as Bisphenol AF or Bisphenol A), of accelerators (for instance ammonium, phosphonium, or aminophosphonium salts), and of bivalent metals oxides and/or hydroxides (for instance MgO, Ca(OH)₂).

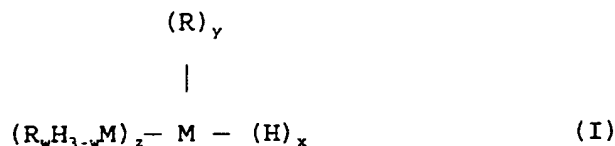
[0004] Peroxide-curable fluoroelastomers have been developed more recently, which contain iodine and/or bromine atoms along the polymeric chain and/or in terminal position. Such iodine and/or bromine atoms can be introduced by suitable iodinated and/or brominated comonomers, or by using during the polymer preparation iodinated and/or brominated chain transfer agents (see for instance US patents 4,243,770, 4,501,869 and 4,745,165). In the presence of free radicals, coming for instance from a peroxide, the iodine and/or bromine atoms act as cure-sites owing to the homolytic scission of the carbon-halogen bonds.

[0005] Since the homolytic scission of C-I bonds is much faster than that of C-Br bonds, the fluoroelastomers containing iodine show much higher curing rates than those of the brominated products. On the other hand the greatest transience of the C-I bonds involves problems in the use and in the conservation of the iodinated fluoroelastomers, mainly due to their poor stability to light. Moreover, it is known that toxic volatile by products, in particular CH₃I, are generated during curing, whose cancerogenous potential is notoriously much higher than that of CH₃Br.

[0006] The Applicant has now surprisingly found that the curing rate of the fluoroelastomers containing bromine can be considerably increased by adding to the curing blend a metallorganic compound hydride as hereinafter defined, obtaining at the same time a high crosslinking degree.

[0007] Object of the present invention is therefore a curable fluoroelastomeric composition, comprising:

- (a) a fluoroelastomer containing bromine;
- (b) an organic peroxide, in amounts comprised between 0.1 and 10%, preferably between 1 and 5% by weight with respect to the fluoroelastomer;
- (c) a metallorganic hydride having the formula:



wherein M is selected from Sn, Si, Ge, Pb; x is an integer from 1 to 3; y, z are zero or integers from 1 to 3, with the proviso y + z = 4 - x; w is an integer from 1 to 3; the R groups, equal to or different from each other, are selected from: alkyls C₁-C₄, aryls C₆-C₁₂, arylalkyls and alkylaryls C₇-C₁₄, optionally containing nitrile and/or hydroxyl groups; in amounts comprised between 0.2 and 10%, preferably between 0.5 to 2% by weight with respect to the fluoroelastomer.

[0008] A further object of the present invention consists in a process for the curing of a composition based on a fluoroelastomer containing bromine, which comprises the addition to the composition of an organic peroxide and of an hydride of formula (I) as defined above, in amounts corresponding to the values indicated above, and subsequently the heating of the composition at such a temperature as to cause the decomposition of the peroxide.

[0009] The hydrides of formula (I) are known compounds (see for instance J. Am. Chem. Soc., 116 (1994), page 4521-4522). Particularly preferred are those wherein x = 1 and w = 3, for instance: tri(n-butyl)-tin-hydride, tri(ethyl)silyl-hydride, di(trimethylsilyl)-silylmethyl-hydride, tri(trimethylsilyl)-silylhydride, and the like, or mixtures thereof.

[0010] The fluoroelastomers containing bromine are as well known products. They contain bromine in amounts generally comprised between 0.001 and 5%, preferably between 0.01 and 2.5%, by weight with respect to the total weight

of the polymer. The bromine atoms can be present along the chain and/or in terminal position.

[0011] In order to introduce bromine atoms along the chain, the copolymerization of the basic monomers of the fluoroelastomer is carried out with a suitable bromine-containing fluorinated comonomer (cure-site monomer) (see for instance **US patents 4,745,165, 4,831,085, and 4,214,060**). Such comonomer can be selected for instance from:

(a) bromo(per)fluoroalkyl-perfluorovinylethers having the formula:



wherein R_f is a (per)fluoroalkylene $C_1\text{-}C_{12}$, optionally containing chlorine and/or ether oxygen atoms; for instance: $\text{BrCF}_2\text{-O-CF=CF}_2$, $\text{BrCF}_2\text{CF}_2\text{-O-CF=CF}_2$, $\text{BrCF}_2\text{CF}_2\text{CF}_2\text{-O-CF=CF}_2$, $\text{CF}_3\text{CFBrCF}_2\text{-O-CF=CF}_2$, and the like;

(b) bromo-(per)fluoroolefins having the formula:



wherein R'_f is a (per)fluoroalkylene $C_1\text{-}C_{12}$, optionally containing chlorine atoms; for instance: bromotrifluoroethylene, 1-bromo-2,2-difluoroethylene, bromo-3,3,4,4-tetrafluorobutene-1, 4-bromo-perfluorobutene-1, and the like.

[0012] The units of brominated comonomer in the final polymer are present in amounts generally comprised between 0.01 and 3% by moles, preferably between 0.1 and 1% by moles.

[0013] In replacement of or in addition to the brominated comonomer, the fluoroelastomer can contain bromine atoms in terminal position, deriving from a suitable brominated chain transfer agent introduced in the reaction medium during the polymer preparation, as described in **US patent 4,501,869**.

[0014] Such transfer agents have the formula $R_f\text{Br}_x$, wherein R_f is a x-valent (per)fluoroalkylic radical $C_1\text{-}C_{12}$, optionally containing chlorine atoms, while x is 1 or 2. They can be selected for instance from: CF_2Br_2 , $\text{Br}(\text{CF}_2)_2\text{Br}$, $\text{Br}(\text{CF}_2)_4\text{Br}$, CF_2ClBr , $\text{CF}_3\text{CFBrCF}_2\text{Br}$, and the like. The amount of bromine in terminal position is generally comprised between 0.001 and 3%, preferably between 0.01 and 1%, by weight with respect to the fluoroelastomer weight.

[0015] The basic monomeric structure of the fluoroelastomers containing bromine generally comprises from 20 to 85% by moles of VDF and/or TFE, copolymerized with at least another fluorinated ethylenically unsaturated monomer, selected for instance from: perfluoroolefins $C_3\text{-}C_8$, such as hexafluoropropene (HFP), perfluorobutene; fluoroolefins $C_2\text{-}C_8$ containing hydrogen and/or chlorine, such as trifluoroethylene, pentafluoropropene, chlorotrifluoroethylene (CTFE); (per)fluoroalkylvinylethers (PAVE) $\text{CF}_2\text{=CFOR}_f$, wherein R_f is a (per)fluoroalkyl $C_1\text{-}C_6$, for instance trifluoromethyl, pentafluoropropyl; perfluoro-oxyalkylvinylethers $\text{CF}_2\text{=CFOX}$, wherein X is a perfluoro-oxyalkyl $C_1\text{-}C_{12}$ having one or more ether groups, for instance, perfluoro-2-propoxy-propyl. Units deriving from non fluorinated ethylenically unsaturated monomers, in particular non fluorinated olefins $C_2\text{-}C_8$, such as ethylene and propylene, can be also present.

The curable compositions object of the present invention comprise an organic peroxide. The organic peroxide must be capable of generating free radicals owing to heating or in presence of redox systems. It can be for instance selected from: 2,5-dimethyl-2,5-di(terbutylperoxy)hexane, 2,5-dimethyl-2,5-di(terbutylperoxy)hexano-3, dicumylperoxide, dibenzoylperoxide, di-tert-butylperbenzoate, di-tert-butylperoxide, di[1,3-dimethyl-3-(terbutylperoxy)butyl]-carbonate, and the like. Other usable organic peroxides are described in **US patent 5,153,272**.

[0016] Also polyunsaturated compounds acting as curing co-agents are usually added to the peroxide-curable compositions in amounts generally comprised between 0.1 and 10%, preferably between 0.5 and 5%, by weight with respect to the fluoroelastomer. They can be selected for instance from: triallyl-cyanurate (TAC), triallyl-isocyanurate (TAIC), triallyl-trimellitate, tris(diallylamino)-s-triazine, triallyl-phosphite, N,N-diallyl-acrylamide, hexaallyl-phosphoramidate, N, N'-m-phenylene-bismaleimide, diallyl-phthalate, tri(5-norbornene-2-methylene)-cyanurate, and the like.

[0017] Oxides and/or hydroxides of divalent metals, for instance, Ca, Mg, Pb, or Zn, optionally in association with a salt of a weak acid are usually added to the blend, before curing, in amounts generally comprised between 1 and 15% by weight, preferably between 2 and 10% by weight, with respect to the fluoroelastomer.

[0018] The compositions object of the present invention can moreover contain other conventional additives, such as pigments, stabilizers, antioxidants, thickeners, reinforcing agents, plastifiers, processing aids, etc. Additives of inorganic types are for instance: carbon black, silica, titanium oxide, talc, barium sulphate, and the like. Fibers of polymers containing fluorine, such as polytetrafluoroethylene, polyvinylidene fluoride, polychlorotrifluoroethylene, tetrafluoroethylene/ethylene copolymers, and the like can be used as reinforcing agents.

[0019] The various components of the compositions object of the present invention can be mixed each other and homogenized according to conventional techniques, such as roll mixing, kneader mixing, Banbury mixing, and the like.

The subsequent processing and moulding steps can be carried out, as well, according to known techniques, such as calendaring, extrusion, compression or injection molding, etc.

[0020] The compositions object of the present invention can be cured by simple heating at such a temperature as to cause the decomposition of the organic peroxide, for instance from 100° to 250°C for a time of about 1-120 min. Subsequently the cured articles can be optionally submitted to post-curing processes, so as to eliminate water and other volatile by-products and to stabilize the mechanical and elastic properties, for instance by heating in press at about 150°-300°C for 6-30 hours.

[0021] The present invention will be better illustrated now by the following working examples, whose purpose is merely indicative but not limitative of the scope of the invention.

EXAMPLE 1

[0022] A rubber Tecnoflon^(R) P2 (53% moles of VDF, 23% moles HFP, 24% moles TFE), containing 0.59% by weight of bromine deriving from the introduction of 2-bromo-perfluoroethyl-perfluorovinylether (BVE) as a comonomer, having number average molecular weight equal to 64,000 and weight average molecular weight equal to 250,000, was used for the preparation of the compositions.

[0023] To 100 g of such rubber were added:

- 3 phr (1 phr = 1 g of substance for 100 g of rubber) of peroxide Lupercol^(R) 101 XL (2,5-dimethyl-2,5-di(terbutylperoxy)hexane);
- 4 phr of triallyl-isocyanurate (TAIC);
- 0.536 phr of tri-n-butyl-tin hydride $[\text{CH}_3(\text{CH}_2)_3\text{Sn-H}$ (TBSI);
- 5 phr of ZnO;
- 30 phr of carbon black MT.

[0024] The mixing was carried out by rolls. The blend composition and its Mooney viscosity (standard ASTM D1646-82) are reported in Table 1.

[0025] The curing curve was determined on the composition thus obtained by Oscillating Disk Rheometer (ODR) by Monsanto (100S Model), according to the standard ASTM D2084-81, by operating at 177°C with an oscillation width of 3°. From such curve were calculated the parameters reported in Table 1 relating to the crosslinking rate and degree: M_L (minimum torque); M_H (maximum torque); $M_H - M_L$ (final crosslinking degree); $(M_H - M_L)/M_H$ (normalized value of the crosslinking degree); t_x (x = 2, 10, 50) (time required for an increase of the torque of x lb-inc above M_L); t'_x (x = 50, 90) (time required for an increase of x% of the torque); V_{\max} (maximum crosslinking rate).

EXAMPLE 2 (comparative)

[0026] Example 1 was repeated with the same blend but free from TBSI. The composition and the data concerning the ODR curve are reported in Table 1.

[0027] Comparing the data obtained in Examples 1 and 2, it can be noticed how the presence of TBSI in the curable composition considerably increases the curing rate, with a good final crosslinking degree.

EXAMPLE 3

[0028] Example 1 was repeated by using an amount of 0.536 phr of triethyl-tin-hydride instead of TBSI. The results are reported in Table 1.

EXAMPLE 4

[0029] Example 1 was repeated by using an amount of 0.536 phr of triethyl-silyl-hydride instead of TBSI. The results are reported in Table 1.

TABLE 1

EXAMPLE	1	2(*)	3	4
Blend composition				
Polymer (g)	100	100	100	100

(*) comparative

TABLE 1 (continued)

EXAMPLE	1	2(*)	3	4
<u>Blend composition</u>				
Lupercor ^(R) 101 XL (phr)	3	3	3	3
TAIC (phr)	4	4	4	4
TBSI (phr)	0.536	-	0.536 ⁺⁺	0.536 ⁺⁺⁺
ZnO (phr)	5	5	5	30
Carbon black MT (phr)	30	30	30	
<u>Mooney Viscosity (lb-in)</u> (ASTM 1646-82)	85	87	85	90
<u>Curing curve ODR</u> (177°C, width=3° ASTM D2084-81)				
M _L (lb-in)	21.3	20.2	21.2	24
M _H (°)	79.1	80.1	79	81
M _H -M _L (°)	57.8	59.9	57	58.5
(M _H -M _L)/M _H	0.73	0.75	0.73	0.70
t _{s2} (sec)	63	75	64	74
t _{s10} (")	87	99	88	95
t _{s50} (")	288	318	295	310
t'50 (")	120	144	123	140
t'90 (")	336	405	340	398
V _{max} (lb-in/sec)	0.62	0.53	0.63	0.53

(*) comparative

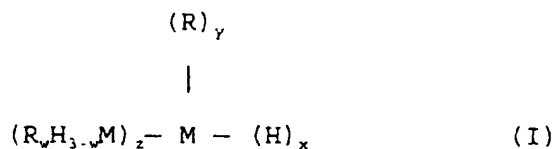
++ triethyl-tin-hydride

+++ triethyl-silyl hydride

Claims

1. Curable fluoroelastomeric composition, comprising:

- (a) a fluoroelastomer containing bromine;
- (b) an organic peroxide, in amounts comprised between 0.1 and 10% by weight with respect to the fluoroelastomer;
- (c) a metallorganic hydride having the formula:



wherein M is selected from Sn, Si, Ge, Pb; x is an integer from 1 to 3; y, z are zero or integers from 1 to 3, with the proviso $y + z = 4 - x$; w is an integer from 1 to 3; the R groups, equal to or different from each other, are selected from: alkyls C₁-C₄, aryls C₆-C₁₂, arylalkyls and alkylaryls C₇-C₁₄, optionally containing nitrile and/or hydroxyl groups; in amounts comprised between 0.2 and 10% by weight with respect to the fluoroelastomer.

2. Composition according to claim 1, wherein the hydride of formula (I) has x = 1 and w = 3.

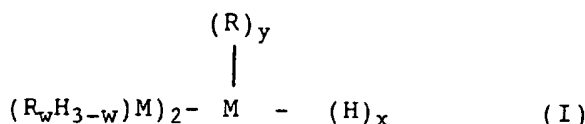
3. Composition according to claim 2, wherein the hydride is selected from: tri(n-butyl)-tin-hydride, tri(ethyl)silyl-hydride, di(trimethylsilyl)-silylmethyl-hydride, tri(trimethylsilyl)-silylhydride, or mixtures thereof.

4. Composition according to anyone of the preceding claims, wherein the fluoroelastomer contains bromine in amounts comprised between 0.001 and 5% by weight with respect to the total weight of the polymer, the bromine atoms being present along the chain and/or in terminal position.
5. Composition according to claim 4, wherein the bromine atoms are along the chain.
6. Composition according to claim 4, wherein the bromine atoms are in terminal position.
7. Composition according to anyone of the preceding claims, wherein the fluoroelastomer has a basic monomeric structure comprising from 20 to 85% by moles of VDF and/or TFE, copolymerized with at least another fluorinated ethylenically unsaturated monomer.
8. Composition according to claim 7, wherein the fluorinated ethylenically unsaturated monomer is selected from: perfluoroolefins C_3-C_8 ; fluoroolefins C_2-C_8 containing hydrogen and/or chlorine; (per)fluoroalkylvinylethers (PAVE) $CF_2=CFOR_f$, wherein R_f is a (per)fluoroalkyl C_1-C_6 ; perfluoro-oxyalkylvinylethers $CF_2=CFOX$, wherein X is a perfluoroxyalkyl C_1-C_{12} having one or more ether groups.
9. Composition according to claims 7 or 8, wherein the fluoroelastomer comprises moreover units deriving from non fluorinated ethylenically unsaturated monomers.
10. Composition according to anyone of the preceding claims, further comprising a polyunsaturated compound acting as a curing co-agent.
11. Composition according to claim 10, wherein the polyunsaturated compound is present in amounts comprised between 0.1 and 10% by weight with respect to the fluoroelastomer.
12. Composition according to claims 10 or 11, wherein the curing co-agent is selected from: triallyl-cyanurate (TAC), triallyl-isocyanurate (TAIC), triallyl-trimellitate, tris(diallylamino)-s-triazine, triallyl-phosphite, N,N-diallyl-acrylamide, hexaallyl-phosphoramidate, N,N'-m-phenylene-bismaleimide, diallyl-phthalate, tri(5-norbornene-2-methylene)-cyanurate.
13. Process for curing a composition based on a fluoroelastomer containing bromine, which comprises adding to the composition an organic peroxide and an hydride of formula (I) as defined in the preceding claims, and subsequently heating the composition at a temperature such as to cause the peroxide decomposition.

Patentansprüche

1. Härtbare Fluorelastomerenzusammensetzung, enthaltend:

- (a) ein Brom enthaltendes Fluorelastomer;
- (b) ein organisches Peroxid in Mengen von 0,1 bis 10 Gew.%, bezogen auf das Fluorelastomer;
- (c) ein metallorganisches Hydrid der Formel:

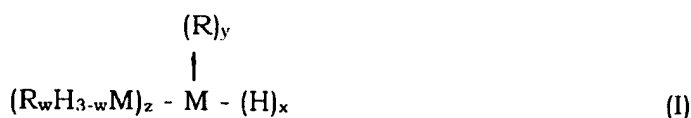


in der M aus Sn, Si, Ge, Pb ausgewählt ist; X eine ganze Zahl von 1 bis 3 ist; Y, Z Null oder ganze Zahlen von 1 bis 3 sind mit der Bedingung: $Y + Z = 4 - X$; W eine ganze Zahl von 1 bis 3 ist; die Gruppen R, die gleich oder voneinander verschieden sind, sind ausgewählt aus: C_1-C_4 -Alkylen, C_6-C_{12} -Arylen, C_7-C_{14} -Arylalkylen und -Alkylarylen, die gegebenenfalls Nitril- und/oder Hydroxylgruppen enthalten; in Mengen zwischen 0,1 und 10 Gew.%, bezogen auf das Fluorelastomer.

2. Zusammensetzung nach Anspruch 1, wobei das Hydrid der Formel (I) $x = 1$ und $w = 3$ besitzt.
3. Zusammensetzung nach Anspruch 2, wobei das Hydrid aus folgenden ausgewählt ist: Tri(n)butyl-zinn-hydrid, Tri(ethyl)silylhydrid, Di(trimethylsilyl)-silylmethylhydrid, Tri(trimethylsilyl)-silylhydrid oder Mischungen daraus.
4. Zusammensetzung nach einem der vorstehenden Ansprüche, wobei das Fluorelastomer Brom in Mengen von 0,001 bis 5 Gew.%, bezogen auf das Gesamtgewicht des Polymeren, enthält, wobei die Bromatome entlang der Kette und/oder in Endstellung vorliegen.
5. Zusammensetzung nach Anspruch 4, wobei die Bromatome entlang der Kette vorliegen.
6. Zusammensetzung nach Anspruch 4, wobei die Bromatome in Endstellung vorliegen.
7. Zusammensetzung nach einem der vorherigen Ansprüche, wobei das Fluorelastomer eine monomere Grundstruktur besitzt, die von 20 bis 85 Mol% VDF und/oder TFE enthält, copolymerisiert mit wenigstens einem anderen fluorierten ethylenisch ungesättigten Monomeren.
8. Zusammensetzung nach Anspruch 7, wobei das fluorierte ethylenisch ungesättigte Monomer ausgewählt ist aus: C_3-C_8 -Perfluoroolefine; C_2-C_8 Fluoroolefine, die Wasserstoff und/oder Chlor enthalten, (Per)fluoroalkylvinylether (PAVE) $CF_2=CFOR_f$, wobei R_f ein C_1-C_6 -(Per)fluoroalkyl ist; Perfluorooxyalkylvinylether $CF_2=CFOX$, wobei X ein C_1-C_{12} -Perfluorooxyalkyl mit einer oder mehreren Ethergruppen ist.
9. Zusammensetzung nach den Ansprüchen 7 oder 8, wobei das Fluorelastomer weiterhin Einheiten umfaßt, die von nicht fluorierten ethylenisch ungesättigten Monomeren abstammen.
10. Zusammensetzung nach einem der vorstehenden Ansprüche, die weiterhin eine mehrfach ungesättigte Verbindung enthält, die als ein die Härtung unterstützendes Mittel wirkt.
11. Zusammensetzung nach Anspruch 10, wobei die mehrfach ungesättigte Verbindung in Mengen zwischen 0,1 und 10 Gew.%, bezogen auf das Fluorelastomer, vorliegt.
12. Zusammensetzung nach den Ansprüchen 10 oder 11, wobei das die Härtung unterstützende Mittel ausgewählt ist aus: Triallyl-cyanurat (TAC), Triallylisocyanurat (TAIC), Triallyl-trimellit, Trisdiallylamino-s-triazin, Triallyl-phosphit, N,N-Diallyl-acrylamid, Hexaallyl-phosphoramid, N,N'-m-Phenylen-bismaleimid, Diallyl-phthalat, Tri-5-norbornen-2-methylen)-cyanurat.
13. Verfahren zur Härtung einer Zusammensetzung auf der Grundlage eines Brom enthaltenden Fluorelastomeren, das den Zusatz eines organischen Peroxids und eines Hydrids der Formel (I), wie in den vorstehenden Ansprüchen definiert, zu der Zusammensetzung und anschließendes Erhitzen der Zusammensetzung auf eine solche Temperatur umfaßt, daß die Zersetzung des Peroxids bewirkt wird.

Revendications

1. Composition fluoroélastomère durcissable comprenant :
 - (a) un fluoroélastomère contenant du brome ;
 - (b) un peroxyde organique, en des quantités comprises entre 0,1 et 10 % en poids par rapport au fluoroélastomère ;
 - (c) un hydruure organométallique ayant la formule



dans laquelle M est choisi parmi Sn, Si, Ge, Pb ; x est un entier de 1 à 3 ; y, z valent zéro ou sont des entiers de 1 à 3, à la condition que $y + z = 4 - x$; w est un entier de 1 à 3 ; les groupes R, identiques les uns aux autres ou différents les uns des autres, sont choisis parmi les groupes alkyle en C₁ à C₄, aryle en C₆ à C₁₂, arylalkyle et alkylaryle en C₇ à C₁₄, contenant éventuellement des groupes nitrile et/ou hydroxyle ; en des quantités comprises entre 0,2 et 10 % en poids par rapport au fluoroélastomère.

2. Composition selon la revendication 1, dans laquelle, dans l'hydrure de formule 1, $x = 1$ et $w = 3$.
3. Composition selon la revendication 2, dans laquelle l'hydrure est choisi parmi l'hydrure de tri(n-butyl)étain, l'hydrure de tri(éthyl)silyle, l'hydrure de di(triméthylsilyl)silylméthyle, l'hydrure de tri(triméthylsilyl)silyle ou leurs mélanges.
4. Composition selon l'une quelconque des revendications précédentes, dans laquelle le fluoroélastomère contient du brome en des quantités comprises entre 0,001 et 5 % en poids par rapport au poids total du polymère, les atomes de brome étant présents le long de la chaîne et/ou en position terminale.
5. Composition selon la revendication 4, dans laquelle les atomes de brome se trouvent le long de la chaîne
6. Composition selon la revendication 4, dans laquelle les atomes de brome se trouvent en position terminale.
7. Composition selon l'une quelconque des revendications précédentes, dans laquelle le fluoroélastomère a une structure monomère de base constituée de 20 à 85 % en moles de VDF et/ou de TFE, copolymérisé avec au moins un autre monomère fluoré à insaturation éthylénique.
8. Composition selon la revendication 7, dans laquelle le monomère fluoré à insaturation éthylénique est choisi parmi les perfluorooléfines en C₃ à C₈ ; les fluorooléfines en C₂ à C₈ contenant de l'hydrogène et/ou du chlore ; les (per) fluoroalkylvinyléthers (PAVE) $CF_2=CFOR_f$, où R_f est un groupe (per)fluoroalkyle en C₁ à C₆ ; les perfluoro-oxyalkylvinyléthers $CF_2=CFOX$ dans lesquels X est un groupe perfluorooxyalkyle en C₁ à C₁₂ ayant un ou plusieurs groupes éther.
9. Composition selon les revendications 7 ou 8, dans laquelle le fluoroélastomère comprend en outre des motifs qui dérivent de monomères non fluorés à insaturation éthylénique.
10. Composition selon l'une quelconque des revendications précédentes, qui comprend en outre un composé polyinsaturé jouant le rôle d'un co-agent de durcissement.
11. Composition selon la revendication 10, dans laquelle le composé polyinsaturé est présent en des quantités comprises entre 0,1 et 10 % en poids par rapport au fluoroélastomère.
12. Composition selon les revendications 10 ou 11, dans laquelle le co-agent de durcissement est choisi parmi le cyanurate de triallyle (TAC), l'isocyanurate de triallyle (TAIC), le trimellitate de triallyle, la tris(diallylamino)-s-triazine, le phosphite de triallyle, le N,N-diallyl-acrylamide, l'hexaallylphosphoramide, le N, N'-m-phénylènebismaléimide, le phthalate de diallyle, le cyanurate de tris(5-norbornène-2-méthylène).
13. Procédé de durcissement d'une composition à base d'un fluoroélastomère contenant du brome, qui consiste à ajouter à la composition un peroxyde organique et un hydrure de formule (I) tel que défini dans les revendications précédentes, puis à chauffer la composition à une température provoquant une décomposition du peroxyde.